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(54) Toilet cleansing gel block

(57) A toilet cleanser comprises a gel block, which is only slowly eroded by flushing water, including a surface active agent and gellan gum gelled by monovalent ions, eg. sodium or potassium.

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GEL

The present invention relates to a gel, and in particular a gel suitable for use as a cleansing preparation.

Considerable research has been carried out into the replacement of widely used cleansing products, such as natural soaps, with surfactant compositions. The use of gels as a base for such composition has been investigated for this purpose, but has proved to be somewhat problematic in terms of the low water solubility properties of most commonly used sufficiently coherent gels. Problems have also been encountered in trying to develop a gel system capable of releasing required amounts of surfactants over a sustained period of time. Thus, for example, where it has been desired to produce a toilet block (that is a lavatory cleaner which erodes slowly as a result of being exposed to flushing water) it has proved difficult to provide a formulation which is both water erodible and coherent (in the sense that it forms a self-supporting mass).

We have now developed a gel which alleviates the above problems.

According to the present invention there is provided a water erodible coherent gel which comprises surfactant and gellan gum gelled by monovalent ions.

Aptly the gel of this invention is for use as a toilet block. Such toilet blocks form a favoured aspect of this invention.

Suitable monovalent ions for use in this invention include potassium, sodium and the like. A particularly preferred ion is potassium since it has been found that

using potassium ions allows the preparation of a clear, transparent gel which offers considerable visual appeal. Preferably, the monovalent ions are either provided by a salt or a surfactant. In the case where the gel contains potassium ions, a preferred source of these ions is tripotassium citrate.

Advantageously, the monovalent ions are present in the gel at a level not greater than 0.5% by weight, based on the weight of the gel, so as to optimise the gelation properties thereof.

The clarity, transparency and erodability properties of a gel according to the present invention can be adversely affected by the presence of multivalent ions, such as calcium or the like. It is preferred, therefore, that the gel is essentially free of multivalent ions. The skilled worker will appreciate that it is most unusual to avoid gelling quantities of multivalent ions in this way since it is normal practice in the art to use multivalent ions to increase gel strength.

Gellan gum refers to the extracellular polysaccharide obtained by the aerobic fermentation of the microorganism, Pseudomonas elodea, in a suitable nutrient medium. Various forms of gellan gum have been described: (U.S.P. 4, 503, 084, Baird et al.) e.g., native, deacetylated, deacetylated clarified, partially deacetylated, and partially deacetylated clarified.

It is preferred that the gellan gum employed in the present gel is a "low acetyl" gellan gum. As used herein, the term "low acetyl" denotes a level of acylation of the gellan gum of 0.3 to 0% by weight.

It is preferred that the gellan gum is present in the gel in an amount of 0.1 to 5% by weight based on the weight of the gel, for example 0.25 to 2.5%. The amount of gellan gum employed in a gel according to the present invention is selected according to the required dissolution properties of the gel. According to a first embodiment of the present invention, the gellan gum is present in an amount of 0.75 to 1.25% by weight based on the weight of the gel. Such gels are only slowly erodible and so may be used where a prolonged dissolution time is required. According to a further preferred embodiment, the gellan gum is present in an amount of 0.5 to 0.6% by weight of the gel, where quicker dissolution of the gel is beneficial.

Preferably the surfactant is anionic surfactant, non-ionic surfactant or a mixture thereof. The presence of an anionic surfactant has been found to be beneficial in providing the desired foaming properties of the gel when used as a cleansing preparation. In a favoured embodiment, the surfactant comprises a mixture of an anionic surfactant and a non-ionic surfactant. This has been found to optimise the foaming and detergent properties of the gel and to maintain gel strength and erodability.

Suitable non-ionic surfactants include polyethoxylated (20) fatty alcohol, polyethoxylated (40) hydrogenated castor oil, primary C9/C11 alcohol ethylene oxide condensates, fatty alcohol C_8-C_{16} glycoside and coconut fatty acid diethanolamide. A particularly preferred non-ionic surfactant is polyethoxylated (20) fatty alcohol.

Suitable anionic surfactants include sodium lauryl sulphate, ammonium lauryl sulphate, triethanolamine lauryl ether sulphate and sodium lauryl ether sulphate.

A particularly preferred anionic surfactant is sodium lauryl sulphate.

In the case where the surfactant consists essentially of a non-ionic surfactant, the surfactant can be present in an amount of not greater than 30% by weight, based on the weight of the gel. In the case where the surfactant consists essentially of an anionic surfactant, it is preferred that the anionic surfactant is present in an amount of not greater than 5% by weight, preferably not greater than 3% by weight, based on the weight of the gel.

In certain preferred systems where a mixture of anionic and non-ionic surfactants are used, the total level of surfactant is advantageously not greater than about 15% by weight, based on the weight of the gel.

In a first preferred embodiment where a mixture of anionic and non-ionic surfactants are used, preferred levels of the respective surfactants are as follows:-
(a) the non-ionic surfactant is present in the surfactant mixture at a level not greater than about 3% by weight based on the weight of the gel, preferably at a level of 0.5 to 1.5% by weight, based on the weight of the gel; and
(b) the anionic surfactant is present at a level of 3 to 4% by weight, based on the weight of the gel.

In a second preferred embodiment where a mixture of anionic and non-ionic surfactants are used, preferred levels of the respective surfactants are as follows:-
(a) the non-ionic surfactant is present at a level of 8.5 to 10% by weight, based on the weight of the gel; and
(b) the anionic surfactant is present at a level of 0.5 to 1.5% by weight, based on the weight of the gel.

A particularly preferred gel according to the present invention comprises 3 to 4% by weight, based on the weight of the gel, of an anionic surfactant, 0.5 to 1.5% by weight, based on the weight of the gel, of a non-ionic surfactant and 0.75 to 1.25% by weight, based on the weight of the gel, of gellan gum.

In the case where the surfactant consists essentially of a non-ionic surfactant, it is preferred that a salt, such as tripotassium citrate is included in the gel at a level of about 0.4 to 0.6% by weight based on the weight of the gel.

The constituents of the gel are normally selected and employed in such a way so as to obviate the formation of cloudy or opaque soft gels. It is particularly preferred that the gel is transparent. This may be achieved as hereinbefore indicated.

The gel may further comprises a fragrance. Typically the fragrance is present in an amount of 0.75% to 1.25% by weight, based on the weight of the gel. The gel may contain a colourant if desired.

Advantageously the gel further comprises a preservative, a preferred preservative being n-propyl p-hydroxybenzoate. The preservative is preferably present in a minor amount in the gel, preferably not greater than 0.2% by weight.

The gel may include hydrocolloids other than gellan gum, suitable such hydrocolloids include xanthan, galactomannan and the like. Typically the further hydrocolloids may be blended with the gellan gum. However, inclusion of such other hydrocolloids is not

preferred since it tends to lead to a deterioration of the visual properties of the gel.

A gel according to the present invention is particularly advantageous for use as a slow release medium in an aqueous environment, and is beneficial in that it comprises a natural hydrocolloid system. The gellan gum erodes slowly so as to release the surfactant. Preferably the gel erodes so as to leave substantially no residue. It is a considerable advantage of this invention that such completely dissoluble gels can be produced.

A preferred use of the gel is as a cleansing preparation, and there is further provided by the present invention a cleansing preparation comprising a gel substantially as hereinbefore described.

A particularly preferred cleansing preparation comprises a toilet (lavatory) cleansing block, and there is still further provided by the present invention a toilet (lavatory) cleansing block comprising a gel substantially as hereinbefore described. The cleansing block is advantageously capable of releasing surfactant for at least 350 flushes of a lavatory, preferably for 350 to 400 flushes, when held under the rim.

The gel has applications as other cleansing preparations, such as household cleaning products, personal care products (such as bath blocks, tablets) and the like, where the use of a transparent, firm gel is advantageous. The present invention will now be further illustrated by the following examples which do not limit the scope of the invention in any way.

The gels of the invention may be prepared by blending the gellan gum and a source of monovalent ions, dispersing in water (preferably deionized water especially in hard water areas), heating to effect solution, adding required surfactants and any other desired agents, placing in a mould and allow to set on cooling.

The present invention will now be further illustrated by the following examples which do not limit the scope of the invention in any way.

Example 1

5.3 Procedure

Gel preparation

All gels were prepared by the following procedure:

(1) Dry blend the gellan gum and potassium citrate, before dispersing in cold deionised water. (Use an appropriate amount of water to off-set that lost by evaporation during make-up). Stir throughout steps 1-6.

(2) Heat to 90°C and hold until a homogenous solution is observed.

(3) Cool to 80°C.

(4) Add the surfactants and cool to 70°C.

(5) Add the fragrance.

(6) Add the preservative.

(7) Pour into appropriate containers and leave to set.

A number of gel formulations were prepared and table 1 shows the effects of various substituents on the formulations.

Table I

FORMULATION %w/w	1	2	3	4	5	6
KELCOGEL PC (71006A)	1	1	1			
KELCOGEL (69070A)				1	1	1
Tripotassium Citrate	0.5	→				
*Rewopol NLS 30	3.6	→				
Mulgofen ON870	1	1	6	1	1	6
BBA Fragrance	1		1		1	
Quest Fragrance		1		1		1
Preservative	0.1	→				
OBSERVATIONS:	Firm Opaque Gel	Firm Opaque Gel	Viscous Paste	Firm Clear Gel	Firm Clear Gel	Viscous Paste

* Added as 100% active

The results in Table I show that clear gel preparations are possible but at low levels of surfactant with KELCOGEL gellan gum. Increasing the free metal ion concentration by adding more anionic surfactant results in a viscous precipitate. The addition of sodium citrate via KELCOGEL PC results in a cloudy gel.

Example 2

Tests were conducted to evaluate:

(1) Gel durability i.e. surfactant release rate.

(2) Dissolution/erosion of the gel.

(3) Melting/dissolution temperatures of the gel.

Test 1 A known weight of gel was placed in a 1000cm^3 beaker and repeatedly flushed with fresh 800cm^3 aliquots of tap water until foaming stopped or our target of 400 flushes was reached. The gel was weighed after every 50 flushes. At the end of the test run, the gel was left to dry overnight and reweighed. The total weight loss was calculated.

Test 2 Fresh samples of the gels used in Test 1 were immersed in tap water at ambient temperature and left for 12 days, then left to dry for 24 hours.
Weights were recorded before and after testing.

Test 3 a) Melting point determination of the gel was carried out using the following procedure. 5g of gel contained in a test-tube was placed in a water-bath. The temperature of the water-bath was gradually raised and the melting temperature range (onset of melting to completely molten) was recorded.

b) Dissolution of the gel was investigated by placing a known weight of gel into a 1L beaker containing 600cm^3, of tap water, which was slowly heated with stirring. The temperature of complete dissolution was recorded.

Formulation 5 in table 1 was investigated

Test 1 Gel durability (surfactant release test)

Initial weight of gel /g = 64.35g	
Weight loss of gel after flushing /g	
No. of flushes: 50	55.76
100	43.92
150	30.39
200	19.22
250	11.50
300	7.50
350	2.80
395	Completely dissolved

Note: Different weight loss may be a function of surface area/volume ratio.

Test 2 Dissolution/erosion test

The gel had completely dissolved within 48 hours at ambient temperature.

Test 3

a) Melting point determination

Gel started melting at 65°C
Gel completely molten at 70°C

b) Gel dissolution tests

Gel starts dissolving at 60°C
Gel completely dissolved at 67°C

Example 3

Further gels were prepared according to the method described in Example 1 to investigate the use of higher levels of non-ionic surfactants with lower levels of anionic surfactant. The following table lists the gels prepared.

FORMULATION %w/w	1	2	3	4	5	6	7	8
KELCOGEL (93197A)	1	.....						>
Tripotassium Citrate	0.5	.....						>
Preservative	0.1	.....						>
BBA Fragrance	1	.....						>
Cremophor RH40	9	9	8	8				
Synperonic 9/11					9	9	8	8
*Texapon ALS/1S	1		2		1		2	
*Texapon NA		1		2		1		2
OBSERVATION:	Clear+ Firm Gel		Viscous paste Cloudy		Clear Firm Gel		Viscous paste Cloudy	

* Added as 100% active

The results show that clear firm gels were prepared using a mixed surfactant system, but only in the ratio of 9:1 (9 parts non-ionic, 1 part anionic). Increasing the ratio to 2 parts anionic resulted in very soft gels which collapsed on touch. Therefore the free metal ions need to be at an optimum concentration to give required gel characteristics.

Example 4

The following gels containing 1% anionic and 9% non-ionic were subjected to the tests described in Example 2.

Gel A contains 1% Texapon NA and 9% Cremophore RH40

Gel B contains 1% Texapon NT and 9% Synperonic 91/20

Gel C contains 1% Texapon ALS/1S and 9% Synperonic 91/20

Test 1 Gel durability (surfactant release test)

Initial Weight of gel /g		Gel A (126.37)	Gel B (121.76)	Gel C (86.18)
		Weight loss of gel after flushing /g		
		A	B	C
No.of flushes	50	3.02	0	0.36
	100	6.31	4.06	0.60
	150	8.46	6.36	6.78
	200	14.13	23.17	8.41
	250	21.12	32.69	1.01
	300	21.84	35.26	11.74
	350	22.35	39.45	15.71
	400	24.20	40.69	19.70
Overnight drying		40.51	47.61	28.21
Total % Weight Loss		53%	39%	23%

Note: Different % weight loss may be a function of surface area/volume ratio.

Test 2

	Gel A	Gel B	Gel C
Initial weight (g)	44.06	83.27	106.67
Weight (g) After 12 days immersed in water and 1 day drying	30.20	57.46	94.60
Total %weight loss	30%	31%	11%

Test 3 - Gel A was used for both tests.

(a) Melting point determination

Gel A started melting at 69°C

Gel A completely molten at 75°C

(b) Gel dissolution tests

Gel B starts dissolving at 55°C

Gel B completely dissolved at 60°C

The in-use test results show that the 10% mixed surfactant gels all foamed very well up to 250 flushes. From 250-400 flushes the foam was present only whilst the gel was being sprayed with water and dispersed quickly once the water flow stopped. The gels were not easily broken up by spraying i.e. they had high gel strength.

The average weight loss of the gel after flushing was 40% compared to 22% for the gels not flushed.

The melting point of the gel was in the range of 69-75°C and complete gel dissolution occurred in water at 55-60°C. Overall the in use test showed that complete dissolution and erosion of this type of gel does not occur at ambient temperature.

CLAIMS:

1. A water erodible coherent gel which comprises surfactant and gellan gum gelled by monovalent ions.

2. A gel according to Claim 1, which is a transparent gel wherein said monovalent ions comprise potassium ions.

3. A gel according to Claim 2, wherein a source of said monovalent ions comprises tripotassium citrate.

4. A gel according to Claim 1, wherein said gellan gum is present in the gel in an amount of 0.1 to 5% by weight based on the weight of the gel.

5. A gel according to Claim 1, wherein said surfactant is anionic surfactant, non-ionic surfactant or a mixture thereof.

6. A gel according to Claim 1, wherein said surfactant comprises a mixture of an anionic surfactant and a non-ionic surfactant.

7. A gel according to claim 1, which further comprises a salt of gelling monovalent ions and a sequestrant of divalent ions.

8. A gel according to Claim 1, which further comprises a fragrance.

9. A gel according to claim 1, which comprises:-
(a) 0.1 to 5% of gellan gum;
(b) 0.5 to 1.5% of non-ionic surfactant;
(c) 3 to 4% of anionic surfactant;
(d) 0.4 to 0.6% of a salt of gelling monovalent ions and a sequestrant of divalent ions; and
(e) 0.75 to 1.25% of a fragrance;
by weight, based on the weight of the gel.

10. A gel according to claim 1, which comprises:-
(a) 0.1 to 5% of gellan gum;
(b) 8.5 to 10% of non-ionic surfactant;
(c) 0.5 to 1.5% of anionic surfactant;
(d) 0.4 to 0.6% of a salt of gelling monovalent ions and a sequestrant of divalent ions;
(e) 0.75 to 1.25% of a fragrance;
by weight, based on the weight of the gel.

11. A cleansing preparation which comprises a water erodible coherent gel which comprises surfactant and gellan gum gelled by monovalent ions.

12. A cleansing preparation according to Claim 11, which comprises a toilet cleansing block.

13. A method of preparing a water erodible coherent gel, which method comprises blending gellan gum and a source of monovalent ions, dispersing the blend in water to produce an aqueous dispersion, heating said dispersion to effect solution and adding surfactants thereto, placing in a mould and allowing to set on cooling.

14. A method according to Claim 13, wherein a source of monovalent ions comprises tripotassium citrate.

15. A method according to Claim 13, wherein the surfactant comprises a mixture of an anionic surfactant and a non-ionic surfactant.

16. A method according to Claim 13, which further comprises adding a fragrance to a solution of gellan gum and monovalent ions.

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Patents Act 1977
Examiner's report to the Comptroller under Section 17
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6 JULY 1995

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE: WPI

Documents considered relevant following a search in respect of Claims :-
1

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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Category	Identity of document and relevant passages	Relevant to claim(s)
A	US 4503084 A (BAIRD ET AL) whole document	1 at least

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